## Fungal Leaching of Titanium from Rock

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Penicillium simplicissimum solubilized up to 80% of the titanium in granitic rocks but less than 2% of the titanium in basaltic rocks.

We have been investigating the interactions of microorganisms with rocks and minerals of the biosphere in studies aimed at developing experiments for the detection of extraterrestrial life. As reported previously (3), the fungus Penicillium simplicissimum (Oudemans) Thom strain WB-28, isolated from the surface of a weathering basalt, produced acid which solubilized significant quantities of the common rock-forming elements silicon, aluminum, iron, and magnesium of several igneous and metamorphic rocks and altered the infrared absorption spectra of some of the residual rock material. To our knowledge, biological leaching of titanium, another of the common rock-forming elements, has never been reported. We now report on the ability of P. simplicissimum WB-28 to leach titanium from a number of igneous and metamorphic rocks.

P. simplicissimum WB-28 was grown in triplicate with 500 mg of powdered sterilized rock in 50 ml of the basal mineral salts solution of Pope and Skerman (4) modified by substituting ammonium molybdate (583  $\mu$ g/liter) for titanium chloride and adding glucose and yeast extract to final concentrations of 4 and 0.01%, respectively. Triplicate controls consisted of uninoculated sterile medium with sterile rock. The initial pH in all flasks was adjusted to 7.0. All rocks were ground to <200 mesh, except basalt A which was <325 mesh. Their partial or complete analyses have been published (1, 3).

Incubation was in air in 250-ml plastic Erlenmeyer flasks at 30 C for 7 days on a rotary shaker (2.5-cm excursion diameter, 320 rev/min). After incubation, the contents of all flasks were brought to 100 ml with distilled water, and the mixture of mycelium and residual leached rock was removed by centrifugation in plastic ware. The supernatant fluid was filtered through Whatman no. 42 filter paper, followed by filtration through a 0.20-µm membrane filter into plastic bottles. Controls were treated in the same manner. These solutions were then analyzed for soluble titanium by atomic absorption spectrophotometry.

Among the rocks tested, not all were equally

susceptible to fungal solubilization of titanium (Table 1). No soluble titanium was detected in the flasks containing rhyolites D-100050 and D-100051 and granite D-100012 probably because the initial titanium content of these rocks (<50 µg of titanium/100 mg of rock) was too low for detectable quantities to appear in solution. The titanium-bearing minerals in mafic rocks of volcanic origin, such as the basalts and andesite, proved quite resistant to fungal attack. Less than 2% of the titanium in these rocks appeared in solution. In contrast, *P. simplicissimum* WB-28 solubilized between 14.2 and 80.9% of the titanium in the more felsic rocks such as

TABLE 1. Solubilization of the titanium of rocks by Penicillium simplicissimum WB-28 after 7 days of incubation at 30 C

Sample	Titanium			
	Rock analysis (µg/100 mg of rock)	In solution <sup>a</sup>		Final pH
		Amt (µg/100 mg of rock)	Per cent	
Basalt				
A	1,079	17.0	1.6	2.66
BCR-1	1,349	12.8	0.9	2.49
D-100043	1,391	10.4	0.7	2.90
Andesite		İ		
AGV-1	629	Nil	Nil	2.55
Granodiorite				
GSP-1	396	56.2	14.2	2.35
Granite	İ			
G-2	282	118.8	42.1	2.36
D-100012	30	Nil	Nil	2.31
D-100018	78	26.0	33.3	2.27
D-100429	102	82.6	80.9	2.27
D-100643	120	90.0	75.0	2.29
Rhyolite				
D-100050	24	Nil	Nil	2.35
D-100051	48	Nil	Nil	2.08
Quartzite				1
D-100316	372	83.4	22.4	2.25
D-100314	408	88.4	21.7	2.66

<sup>&</sup>lt;sup>a</sup> Data for soluble titanium and pH are the means of triplicate cultures. No titanium was detected in sterile uninoculated controls.

granodiorite, granite, and quartzite, despite titanium contents much lower than the mafic rocks.

Among the felsic rocks tested, the quantity of titanium solubilized appeared related to the total titanium content of the rock. The linear correlation coefficient (r = 0.85) calculated from the data in Table 1 for the five granites indicated a strong positive correlation between the initial titanium content and the amounts solubilized. Thus, biogenic solubilization of titanium does not appear to be a function solely of the titanium content of the rock but probably reflects differences in the susceptibility to fungal attack of different titanium-bearing minerals in felsic and mafic rocks. In addition, differences in the grain size of titanium-bearing minerals in the coarsegrained felsic rocks and finer grained mafic rocks probably affect the availability of these minerals to fungal attack.

Loughnan (2), in considering the fate of titanium during the weathering of silicate minerals, concluded that Ti<sup>4+</sup> may show limited mobility if released from the parent minerals as Ti(OH)<sub>4</sub> in an environment with a pH below 5 but would remain immobile if present as TiO<sub>2</sub> until the environmental pH reached a value below 2.5. P. simplicissimum WB-28 produced acid during growth with the rocks tested. Final pH values were below 3 in all cases (Table 1). This suggests that the titanium-bearing minerals in mafic rocks were either resistant to fungal attack or, if at-

tacked, released their Ti<sup>4+</sup> as the more insoluble TiO<sub>2</sub>. The reverse would hold for the felsic rocks, that is, the presence of titanium-bearing minerals susceptible to fungal attack and release of titanium from the parent minerals as the more soluble Ti(OH)<sub>4</sub>.

The artificialities of the experimental system (pure culture, high glucose concentration, finely divided rock, etc.) preclude direct extrapolation of the results in Table 1 to rocks in the natural environment. However, over geological time in regions with warm temperatures and abundant vegetation and rainfall, the associated microflora present during soil formation may well influence the nature and quantity of titanium-bearing minerals in soils developing from felsic as opposed to mafic rocks. Finally, biological leaching may prove feasible for the recovery of titanium from low-grade ores or the waste materials from conventional mining, as is the case for a number of other valuable metals (5).

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